

DECLARATION

I, Kana NOMOTO, residing at c/o PREZIO IP Firm,
Daikanyama TK Bldg. 1F, 2-17-16, Ebisu-Nishi, Shibuya-ku,
Tokyo 150-0021 Japan, solemnly and sincerely declare that
I well understand both Japanese and English languages and
the attached English version is a full, true and faithful
translation of the certified copy of Japanese Patent
Application No. 2002-303631 filed on October 17, 2002.

And I made this solemn declaration conscientiously
believing the same to be true.

Dated this 4th day of July, 2005

Kana Nomoto

Ms. Kana NOMOTO

JAPAN PATENT OFFICE

This is to certify that the annexed is a true copy of
the following application as filed with this office.

Date of Application: October 17, 2002

Application Number : Patent Application No. 2002-303631

Applicant : NEC Electronics Corporation

August 22, 2003

Commissioner, Japan Patent Office
Yasuo IMAI (sealed)

Serial No. P2003-3068826

[Document] Application for Patent
[Docket Number] 74112769
[Filing Date] October 17, 2002
[To] Commissioner, Patent Office
[International Patent Classification] H01L 21/304
[Inventor]
[Address or Domicile] c/o NEC Corporation
7-1, Shiba 5-chome, Minato-ku Tokyo
[Name] Tatsuya SUZUKI
[Inventor]
[Address or Domicile] c/o NEC Corporation
7-1, Shiba 5-chome, Minato-ku Tokyo
[Name] Hidemitsu AOKI
[Applicant for Patent]
[Identification Number] 000004237
[Name] NEC CORPORATION
[Agent]
[Identification Number] 100110928
[Patent Attorney]
[Name] Shinji HAYAMI
[Telephone Number] 03-3461-3687
[Indication of Official Fees]
[Advance Deposit Record Number] 138392
[Amount Paid] ¥21,000
[List of Materials Submitted]
[Material Name] Specification 1
[Material Name] Drawings 1
[Material Name] Abstract 1
[Number of General Power of Attorney] 0110433
[Request for PROOF] Requested

[DOCUMENT] SPECIFICATION

[TITLE OF THE INVENTION] METHOD FOR MANUFACTURING
SEMICONDUCTOR DEVICE AND SEMICONDUCTOR DEVICE

[CLAIMS]

5 1. A method for manufacturing a semiconductor device,
comprising:

forming a patterned film on said semiconductor
substrate, said patterned film having a predetermined
geometry; and

10 after said forming said patterned film, wet-processing
the surface of the semiconductor substrate that has an
exposed surface of a semiconductor material with a chemical
solution containing an organic solvent as a main component.

2. A method for manufacturing a semiconductor device,
15 comprising:

forming a film on a semiconductor substrate;
removing at least a part of said film with a chemical
solution containing an organic solvent as a main component;
and exposing at least a part of the surface of said
20 semiconductor substrate.

3. A method for manufacturing a semiconductor device,
comprising:

forming a insulating film on a semiconductor substrate;
forming a conductive film on said insulating film;
25 forming a patterned protective film on said conductive

film, said patterned protective film having a predetermined geometry;

selectively removing said conductive film utilizing the protective film as a mask;

30 selectively removing said insulating film to partially expose said surface of said semiconductor substrate; and conducting a wet processing for the semiconductor substrate with a chemical solution containing an organic solvent as a main component.

35 4. The method according to claim 3, wherein said selectively removing said insulating film includes:

removing said protective film before partially exposing said surface of said semiconductor substrate.

5. The method according to claim 3 or claim 4, wherein 40 said forming said insulating film includes:

forming a high-k insulating film composed of a material having higher dielectric constant than the silicon oxide film, and said removing said insulating film includes:

45 selectively removing a part of said high-k insulating film via a dry etching utilizing said protective film as a mask;

removing said protective film; and

50 selectively removing the remained part of said high-k insulating film via a wet etching utilizing said conductive film as a mask to partially expose said surface of said

semiconductor substrate,

55 said wet etching being carried out by using a removing solution containing an organic solvent as a main component and a fluoride-containing compound, a removing solution containing hot phosphoric acid or a removing solution containing sulfuric acid.

6. A method for manufacturing a semiconductor device, comprising:

60 forming a insulating film on a semiconductor substrate, said insulating film comprising at least a high-k insulating film that has higher dielectric constant than a silicon oxide film;

65 selectively removing said insulating film via a wet etching with a chemical solution containing an organic solvent as a main component to partially expose said surface of said semiconductor substrate.

7. A method for manufacturing a semiconductor device, comprising:

70 forming a first film and a second film in a first region and a second region, respectively, on a semiconductor substrate;

75 forming a protecting film that covers said second insulating film;

removing said first insulating film to expose the surface of said semiconductor substrate in said first region;

removing said protective film with a chemical solution containing an organic solvent as a main component;

80 forming a third insulating film on said first region, said third insulating film having different thickness or different composition from said second insulating film.

8. The method according to claim 7, wherein said first insulating film, said second insulating film, and said third insulating film may be formed by oxidizing said semiconductor substrate in the respective corresponding regions.

85 9. The method according to claim 7 or claim 8, further comprising:

forming a first high-k insulating film and a second high-k insulating film on said third insulating film and said second insulating film, respectively, said first high-k insulating film and said second high-k insulating film being composed of a material having higher dielectric constant than a silicon oxide film.

10. The method according to any one of claims 1 to 9, wherein said organic solvent is a solvent having polar group.

95 11. The method according to any one of claims 1 to 10, wherein said organic solvent is selected from the group consisting of: isopropyl alcohol; ethylene glycol; 2-heptanone; cyclopentanone; methylethyl ketone; glycol ether; propyleneglycol monomethyl ether; and propyleneglycol monomethyl acetate.

12. The method according to any one of claims 1 to 11, wherein said organic solvent is isopropyl alcohol.

13. The method according to any one of claims 1 to 12, wherein said organic solvent is isopropyl alcohol, and said 105 chemical solution contains not less than 90 % vol. of isopropyl alcohol.

14. A semiconductor device comprising:

110 a semiconductor substrate; and
a first gate insulating film and a second insulating film formed in different regions, respectively, on said semiconductor substrate,

wherein said first gate insulating film comprises a first insulating film and a first high-k film formed on said first insulating film,

115 wherein said second gate insulating film comprises a second insulating film and a second high-k film formed on said second insulating film, the second insulating film having a different thickness or a different material than that of the first insulating film, and

120 wherein said first high-k film and said second high-k film are formed of zirconium, hafnium, lanthanoid, aluminum, indium, gallium or the oxides thereof, and have higher dielectric constant than a silicon oxide film.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Field of the Invention]

The present invention relates to a method for
5 manufacturing a semiconductor device and a semiconductor
device. More specifically, the present invention relates to
a method for manufacturing a semiconductor device in which a
film is deposited on a semiconductor substrate, and a method
for manufacturing a semiconductor device comprising exposing
10 at least a part of the semiconductor substrate during a
process for manufacturing the semiconductor device.

[0002]

[Description of the Related Art]

In recent years, for the purpose of satisfying the
15 increased needs for obtaining higher level of the integration
for semiconductor devices, a type of semiconductor device
(referred as "multi-oxide") is developed, which comprises
various types of devices including gate insulating films
having different thickness. General method for manufacturing
20 conventional semiconductor device having multi-oxides will be
described in reference to Figs. 8 and 9.

[0003]

As shown in Fig. 8A, a device separating region 112 is
formed on a silicon substrate 110, and thereafter an oxide
25 film 114 and an oxide film 116 are formed thereon via a
thermal oxidization. Consecutively, a resist layer 118 is
formed on the oxide film 116, as shown in Fig. 8B.

[0004]

The resultant substrate having films thereon is then
30 wet-etched by using an etch solution such as buffered
hydrofluoric acid (BHF), as shown in Fig. 8B. The operation
provides that the oxide film 114 is removed, as shown in Fig.
8D. Then, the resultant substrate having films thereon is
processed with a removing agent, as shown in Fig. 9A, and the
35 resist layer 118 is removed, as shown in Fig. 9B. Then, as
shown in Fig. 9C, the silicon substrate surface is cleaned
with ammonia-hydrogen peroxide mixture (APM) to remove the
particulate contaminants, and after that the residual metals
and so on are removed by using diluted hydrofluoric acid
40 (DHF).

[0005]

Subsequently, an oxide film 122 is formed via a thermal
oxidization, as shown in Fig. 9D. This processing provides
that two gate insulating films 126 and 128 having different
45 thickness are formed.

[0006]

[PATENT DOCUMENT 1]

JP-A-2000-3,965 (pp. 3, Figs. 57 to 62)

[NON-PATENT REFERENCE 1]

50 "Ultra Clean ULSI Technology" of OHMI, Tadahiro
(written in Japanese), 1995, BAIFUKAN, Tokyo Japan (pp. 156
to 157).

[0007]

[PROBLEM TO BE SOLVED BY THE INVENTION]

55 In general, the removing solution for removing organic
compounds such as resist layer 118 contains sulfuric acid
hydrogen peroxide solution mixture (SPM) including sulfuric
acid as a main component, that is heated at a temperature of
not lower than 100 degree. C (see, for example, NON-PATENT
60 REFERENCE 1). However, when the SPM containing sulfuric acid
and hydrogen peroxide for removing the resist layer 118, an
unwanted chemical oxide film 120 is formed on the surface of
the silicon substrate 100 as shown in Fig. 9B, causing
difficulty in controlling the thickness of the formed gate
65 insulating film to be thinner. Also, when moisture remains
on the surface of the silicon substrate 100, stains such as
watermark or the like is formed, causing difficulty in
controlling the uniformity of the quality of the formed film.

[0008]

70 Meanwhile, the recent technical progress in the
miniaturization of the semiconductor devices requires
improving the switching rate of transistors by designing the
transistor to have a shorter gate length. In order to
provide shorter gate length for the transistor, the thickness
75 of the gate insulating film should be formed to have thinner
film thickness, and therefore a technology for controlling
the film thickness of the formed film to be thinner is
required.

[0009]

80 Further, while the technology for providing the film
thickness of the formed film to be thinner is required, the

device design of having shorter gate length of the transistor causes a problem, in which the gate leakage electrical current increases to a considerable level. Thus, it is 85 expected to solve the problem by employing a conventionally used insulating film having higher dielectric constant than silicon oxide (SiO_2) film (hereinafter referred as "high-k film") to provide physically thicker film while maintaining the dielectric properties thereof.

90 [0010]

However, the low-k film generally involves a problem of having lower thermal resistance, and thus when a high-k film is formed directly on the silicon substrate, a chemical reaction between the high-k film and the surface of the 95 silicon substrate during a thermal processing to deteriorate the device properties. Therefore, it is proposed to provide a silicon oxide film between the high-k film and the silicon substrate to inhibit such deterioration of the device properties (see, for example, JP-A-2001-274,378). In this 100 case, the thickness of the formed silicon oxide film is preferably controlled to have thinner film thickness as possible, in order to maintain the driving capacity of the gate.

[0011]

105 In view of the above situation, the present invention provides a solution to the above-mentioned problems, and it is an object of the present invention to provide a technology of controlling the thickness of the silicon oxide film formed

on the semiconductor substrate to be thinner. It is another
110 object of the present invention to prevent the formation of
the unwanted film or the stain such as watermark on the
semiconductor substrate. It is yet other object of the
invention to provide a technology of controlling the
uniformity of the film formed on the semiconductor substrate.

115 [0012]

[MEANS FOR SOLVING PROBLEM]

According to one aspect of the present invention, there
is provided a method for manufacturing a semiconductor device,
comprising: forming a patterned film on a semiconductor
120 substrate, the patterned film having a predetermined
geometry; after the forming the patterned film, wet-
processing the surface of the semiconductor substrate that
has an exposed surface of a semiconductor material with a
chemical solution containing an organic solvent as a main
125 component.

[0013]

The semiconductor substrate according to the present
invention may comprise: an element semiconductor such as Si,
Ge, or the like; a compound semiconductor such as GaAs, GaN,
130 InP, CdS, SiC, or the like; or a mixed crystal semiconductor
such as InGaAs, HgCdTe or the like. The term "surface of the
semiconductor substrate" indicates a working surface of the
semiconductor substrate. The term "main component" means the
component having the largest volume content in the chemical
135 solution. here, the chemical solution may mainly contain a

nonaqueous solvent. The chemical solution may contain water, and may preferably be free of hydrofluoric acid-containing component, sulfuric acid-containing component or hydrogen peroxide aqueous solution. The wet-processing may be carried 140 out at an ambient temperature. Here, the term "wet-processing" indicates a processing of, for example, rinse processing, cleaning or wet etching for the semiconductor substrate.

[0014]

145 The configuration described above provides preventing the adhesion of water on an exposed surface of the semiconductor substrate when the exposed surface appears, and therefore the formation of unwanted films or watermarks on the semiconductor substrate surface can be prevented.

150 [0015]

According to another aspect of the present invention, there is provided a method for manufacturing a semiconductor device, comprising: forming a film on a semiconductor substrate; removing at least a part of the film with a 155 chemical solution containing an organic solvent as a main component; and exposing at least a part of the surface of the semiconductor substrate.

[0016]

This configuration provides a prevention of forming an 160 unwanted film such as a chemical oxide film on the semiconductor substrate when the semiconductor surface of the semiconductor substrate is partially exposed by the

processing of removing the film on the semiconductor substrate.

165 [0017]

According to further aspect of the present invention, there is provided a method for manufacturing a semiconductor device, comprising: forming a film on a semiconductor substrate; partially removing the film to expose a part of the surface of the semiconductor substrate; and conducting a wet processing for the semiconductor substrate with a chemical solution containing an organic solvent as a main component. In this method, the wet processing for the semiconductor substrate with a chemical solution containing an organic solvent as a main component can be conducted after exposing a part of the surface of the semiconductor substrate without conducting a cleaning processing for the semiconductor substrate with pure water.

[0018]

180 According to yet other aspect of the present invention, there is provided a method for manufacturing a semiconductor device, comprising: forming a first film and a second film on a semiconductor substrate; removing at least a part of the first film to expose a part of the surface of the semiconductor substrate; and removing the second film with a chemical solution containing an organic solvent as a main component. The second film may be a resist layer, for example. The first film may be a gate insulating film, for example.

190 [0019]

In the method according to the present invention, the semiconductor substrate may include a first region and a second region, and the first film and the second film may be formed in the first region and the second region, respectively. In addition, the second region may be protected by the second film formed thereon during the formation process of a device in the first region, and after the formation of the device in the first region, the second film may be removed and other device may be formed in the second region. In such case, since the second film is removed by the organic solvent, the formation of an unwanted film such as a chemical oxide film on the surface of the semiconductor substrate may be prevented, even if the first region on the surface of the semiconductor substrate is exposed during the removal processing for the second film.

205 [0020]

In this method according to the present invention, the second film having a predetermined geometry may be formed on the first film, and the first film may be selectively removed to expose at least a part of the surface of the semiconductor substrate, so that the first film has the predetermined geometry. As such, since the second film is removed by the organic solvent, the formation of an unwanted film such as a chemical oxide film on the surface of the semiconductor substrate may be prevented, even if the surface of the semiconductor substrate is exposed during the removal

processing for the second film.

[0021]

According to yet other aspect of the present invention,
220 there is provided a method for manufacturing a semiconductor
device, comprising: forming a insulating film on a
semiconductor substrate; forming a conductive film on the
insulating film; forming a patterned protective film on the
conductive film, the patterned protective film having a
225 predetermined geometry; selectively removing the conductive
film utilizing the protective film as a mask; selectively
removing the insulating film to partially expose the surface
of the semiconductor substrate; and conducting a wet
processing for the semiconductor substrate with a chemical
230 solution containing an organic solvent as a main component.

[0022]

The protective film may be formed of a resist layer.
The insulating film may be formed of an oxide film or a
nitride film. When the semiconductor substrate is a silicon
235 substrate or a SiC substrate, the insulating film may be
silicon oxide film or silicon nitride film.

[0023]

In the manufacturing method for the semiconductor
device according to the present invention, the removing the
240 insulating film may include removing the protective film
before partially exposing the surface of the semiconductor
substrate.

[0024]

In the manufacturing method for the semiconductor
245 device according to the present invention, the removing the
insulating film may include: selectively removing a part of
the insulating film via a dry etching utilizing the
protective film as a mask; removing the protective film; and
selectively removing the remained part of the insulating film
250 via a wet etching utilizing the conductive film as a mask, to
partially expose the surface of the semiconductor substrate.

[0025]

In the manufacturing method for the semiconductor
device according to the present invention, the forming the
255 insulating film may include: forming a first insulating film;
forming a second insulating film on the first insulating film,
the second insulating film being composed of a material
having higher dielectric constant than the silicon oxide film.

[0026]

260 In the manufacturing method for the semiconductor
device according to the present invention, the removing the
insulating film may include: selectively removing a part of
the second insulating film via a dry etching utilizing the
protective film as a mask; removing the protective film; and
265 selectively removing the remained part of the insulating film
and the first insulating film via a wet etching utilizing the
conductive film as a mask, to partially expose the surface of
the semiconductor substrate. The etching solution for wet-
etching the remaining part of the insulating film may be
270 alcohol, phosphoric acid or sulfuric acid that additionally

contain a fluoride-containing compound.

[0027]

The manufacturing method for the semiconductor device according to the present invention may additionally include
275 forming a device separating region on the semiconductor substrate before conducting the forming the insulating film, and thus, on the device separating region, the surface of the material of the semiconductor substrate can be exposed in the step of removing the insulating film.

280 [0028]

In the manufacturing method for the semiconductor device according to the present invention, the forming the insulating film may additionally include forming a high-k insulating film composed of a material having higher
285 dielectric constant than the silicon oxide film, and the removing the insulating film may additionally include steps of: selectively removing a part of the high-k insulating film via a dry etching utilizing the protective film as a mask; removing the protective film; and selectively removing the
290 remained part of the high-k insulating film via a wet etching utilizing the conductive film as a mask to partially expose the surface of the semiconductor substrate, and the wet etching may be carried out by using a removing solution containing an organic solvent as a main component and a
295 fluoride-containing compound, a removing solution containing hot phosphoric acid or a removing solution containing sulfuric acid. This configuration provides that, if the

semiconductor substrate includes a device separating region formed thereon, the high-k insulating film can be selectively removed without etching the device separating region.

[0029]

According to another aspect of the present invention, there is provided a method for manufacturing a semiconductor device, comprising: forming a insulating film on a semiconductor substrate, the insulating film comprising at least a high-k insulating film that has higher dielectric constant than the silicon oxide film; selectively removing the insulating film via a wet etching with a chemical solution containing an organic solvent as a main component to partially expose the surface of the semiconductor substrate.

[0030]

This manufacturing method for the semiconductor device according to the present invention may additionally include forming a device separating region on the semiconductor substrate before conducting the forming the insulating film, and thus, on the device separating region, the surface of the material of the semiconductor substrate may be exposed in the removing the insulating film. This configuration provides that the high-k insulating film can be selectively removed without etching the device separating region.

[0031]

According to another aspect of the present invention, there is provided a method for manufacturing a semiconductor device, comprising: forming a first film and a second film in

325 a first region and a second region, respectively, on a semiconductor substrate; forming a protecting film that covers the second insulating film; removing the first insulating film to expose the surface of the semiconductor substrate in the first region; removing the protective film
330 with a chemical solution containing an organic solvent as a main component; forming a third insulating film on the first region, the third insulating film having different thickness or different composition from the second insulating film.

[0032]

335 In this configuration, the first and the second regions may be designed to be device forming regions. Alternatively, the second region is designed to be a gate forming region for I/O port. In such case, the third insulating film may be formed to have thinner thickness than the second insulating
340 film.

[0033]

In the manufacturing method for the semiconductor device according to the present invention, the first, the second, and the third insulating films may be formed by
345 oxidizing the semiconductor substrate in the respective corresponding regions.

[0034]

The manufacturing method for the semiconductor device according to the present invention may additionally include
350 forming a first high-k insulating film and a second high-k insulating film on the third insulating film and the second

insulating film, respectively, the first high-k insulating film and the second high-k insulating film being composed of a material having higher dielectric constant than the silicon 355 oxide film.

[0035]

Here, the first high-k insulating film and the second high-k insulating film may be films containing an element of 3A series element, 3B series element or 4A series element. A 360 high-k film may be selected for the films containing an element of 3A series element, 3B series element or 4A series element. The exemplary materials for such films may be zirconium, hafnium, lanthanoid, aluminum, indium, gallium or the oxides thereof. That is, Zr, Hf, Pr, La, Lu, Eu, Yb, Sm, 365 Ho, Ce, Al, In, Ga or the oxides thereof. More specifically, ZrO_x , HfO_x , $HfAlO_x$, Al_2O_3 , In_2O_3 , Ga_2O_3 or the like. In particular, ZrO_x , HfO_x and $HfAlO_x$ are preferable in view of the performances of the resulting devices and the applicability to the manufacturing process. Alternatively, 370 materials having higher dielectric constant than the dielectric constant of the silicon oxide film (3.9 to 4.5), such as barium titanate ($BaSrTiO_3$), titanium oxide (TiO_2), tantalum oxide (Ta_2O_5), silicon nitride (Si_3N_4), silicon oxynitride ($SiON$), alumina (Al_2O_3) or the like.

375 [0036]

In the manufacturing method for the semiconductor device according to the present invention, the organic solvent may preferably be a solvent having polar group. The

polar group is a functional group having electronegativity
380 different from that of carbon, such as hydroxyl group, ether
bond group, carbonyl group, carboxylic group or the like.
The available solvent having polar group may be: alcohols
such as isopropyl alcohol, isobutyl alcohol, ethylene glycol,
tert-butyl alcohol or the like; ethers such as glycol ether,
385 propyleneglycol monomethyl ether or the like; ketones such as
cyclopentanone, cyclohexanone, methylethyl ketone, 2-
heptanone or the like; or esters such as propyleneglycol
monomethyl acetate or the like. Among these, the preferable
solvent may be one or more selected from the group consisting
390 of isopropyl alcohol, ethylene glycol, 2-heptanone,
cyclopentanone, methylethyl ketone, glycol ether,
propyleneglycol monomethyl ether, and propyleneglycol
monomethyl acetate, and in particular isopropyl alcohol is
more preferable. This configuration provides that the
395 formation of unwanted films or stains such as watermarks on
the semiconductor substrate surface can be prevented. In
addition, the solvent may preferably be a hydrophilic solvent.

[0037]

In the manufacturing method for the semiconductor
400 device according to the present invention, the organic
solvent may be isopropyl alcohol, and the chemical solution
may contain not less than 90 % vol. of isopropyl alcohol.

[0038]

In the manufacturing method for the semiconductor
405 device according to the present invention, the protecting

film may be an i-line resist film.

[0039]

In the manufacturing method for the semiconductor device according to the present invention, the protecting 410 layer may be formed of a material that is not dissoluble with buffered hydrofluoric acid.

[0040]

According to another aspect of the present invention, there is provided a method for conducting a wet-processing, 415 comprising: conducting a wet-processing to a semiconductor substrate with a chemical solution containing an organic solvent as a main component when at least a part of a device forming region on the semiconductor substrate is exposed.

[0041]

420 According to another aspect of the present invention, there is provided a method for conducting a wet-processing, comprising: conducting a wet-processing to a semiconductor substrate with a chemical solution containing an organic solvent as a main component to expose the semiconductor 425 substrate.

[0042]

According to another aspect of the present invention, there is provided a semiconductor device comprising: a semiconductor substrate; and a first gate insulating film and 430 a second insulating film formed in different regions, respectively, on the semiconductor substrate, wherein the first gate insulating film comprises a first insulating film

and a first high-k film formed thereon, wherein the second gate insulating film comprises a second insulating film and a 435 second high-k film formed thereon, the second insulating film having a different thickness or a different material than that of the first insulating film, wherein the first high-k film and the second high-k film are formed of zirconium, hafnium, lanthanoid, aluminum, indium, gallium or the oxides thereof, and have higher dielectric constant than a silicon 440 oxide film.

[0043]

In the semiconductor device according to the present invention, the film thickness of the first insulating film 445 may be less than 1nm.

[0044]

[EMBODIMENT OF THE INVENTION]

The specific constitutions according to the present invention will be described below in detail by referring to 450 the attached drawings. In each of the drawings, each of the elements of the semiconductor device will be exaggerated, for the purpose of easily understanding of the present invention.

[0045]

(First Embodiment)

455 Fig. 1 and Fig. 2 show the processing steps for manufacturing a semiconductor device according to the first embodiment of the present invention. In this embodiment, the present invention is applied to the manufacturing of the semiconductor device comprising gate insulating films having

460 different thickness.

[0046]

As shown in Fig. 1A, a device separating region 12 is formed on a silicon substrate 10, and thereafter a first oxide film 14 (having a thickness of, for example, 5.0 nm) 465 and a second oxide film 16 (having a thickness of, for example, 5.0 nm) in a first region 13a and a second region 13b, respectively, via thermal oxidization method. The device separating region 12 is formed via shallow trench isolation method (STI method), and comprises oxide films 470 formed via CVD or thermal oxidization. Subsequently, a resist layer 18 is formed on the second oxide film 16, as shown in Fig. 1B. The resist layer 18 is an i-line resist layer. The formation of the resist layer 18 is carried out by applying an i-line resist material on the second oxide 475 film 16 to form a resist film and conducting a development by exposing the i-line resist film to i-line emitted from, for example, xenon-mercury lamp (not shown) through a patterning mask (not shown) to form the resist layer 18. The resultant multi-layered structure is then wet-etched with buffered 480 hydrofluoric acid (BHF), as shown in Fig. 1C. As a result, the first oxide film 14 is removed as shown in Fig. 1D.

[0047]

Subsequently, as shown in Fig. 2A, isopropyl alcohol (IPA) is applied thereon at an ambient temperature to remove 485 the resist layer 18 via the wet etching. The wet etching may be carried out via a dipping process or via a single wafer

process. In this processing, the resist layer 18 is dissolved into IPA to remove the resist layer 18 as shown in Fig. 2B. Then, particulate contaminants are removed from the 490 surface of the silicon substrate 10 with ammonia-hydrogen peroxide mixture (APM), and thereafter residual metals are cleaned by diluted hydrofluoric acid (DHF). In this occasion, a thin chemical oxide film 20 (having a thickness of, for example, 0.9 nm) is formed on the surface of the silicon 495 substrate (Fig. 2C).

[0048]

Subsequently, as shown in Fig. 2D, a third oxide film 22 (having a thickness of, for example, 0.8 nm) is formed via rapid thermal oxidation (RTO) process. This processing 500 provides that two gate insulating film having different thickness, i.e., the first gate insulating film 26 (having a thickness of, for example, 0.8 nm) and the second gate insulating film 28 (having a thickness of, for example, 5 nm) are formed.

505 [0049]

In this embodiment, the resist layer 18 is removed by using IPA, chemical oxide film is not formed on the surface of the silicon substrate 10 during the removing processing for the resist layer 18, and only a thin chemical oxide film 510 20 is formed during the cleaning process with APM and DHF. As such, in the subsequent process of forming the third oxide film 22 via RTO, the film thickness of the formed film can be controlled to be thinner. Further, this processing prevent

the generation of stains such as watermarks, the uniformity
515 of the quality of the third oxide film 22 can be suitably
controlled. In addition, this enables the processing at an
ambient-temperature with IPA for removing the resist layer 18,
and therefore the gate insulating films having different film
thickness can be formed with high process stability by a
520 simple process.

[0050]

(Second Embodiment)

Fig. 3 and Fig. 4 show the processing steps for
manufacturing a semiconductor device according to the second
525 embodiment of the present invention. In this embodiment, the
present invention is applied to the manufacturing of the
semiconductor device by forming a high-k insulating film on
gate insulating films having different thickness, i.e., the
first gate insulating film 26 and the second gate insulating
530 film 28, as shown in Fig. 2.

[0051]

Similarly as described in the first embodiment in
reference to Figs. 1A to 1D and Figs. 2A to 2E, a first gate
insulating film 26 and a second gate insulating film 28 are
535 formed on the silicon substrate 10 having a device separating
region 12 thereon (Fig. 3A). Subsequently, a high-k
insulating film 30 (having a thickness of, for example, 3 nm)
is deposited via chemical vapor deposition (CVD) such as
atomic-layer chemical vapor deposition (ALCVD), metal-organic
540 chemical vapor deposition (MOCVD) and so on, or via

sputtering. The high-k insulating film 30 may be formed of a material having larger dielectric constant than that of the silicon oxide film (3.9 to 4.5), for example, hafnium oxide (HfO_2), zirconium oxide (ZrO_2), HfAlO_x or the like. Further, 545 a polysilicon 31 (having a thickness of, for example, 20 nm) is deposited on the upper surface of the high-k insulating film 30.

[0052]

Subsequently, a resist layer 32 is formed on the 550 polysilicon 31, as shown in Fig. 3C. Thereafter, the polysilicon 31 and the high-k insulating film 30 are selectively dry-etched through the mask of the resist layer 32 to carry out a stepwise removal. The etching is continued to a halfway to the entire thickness of the high-k insulating 555 film, and thereafter the processing with SPM is carried out.

[0053]

Having this operation, the resist layer 32 is removed, as shown in Fig. 4A. Subsequently, the high-k insulating film 30, the first gate insulating film 26 and the second 560 gate insulating film 28 are selectively removed via the wet-etching through the mask of the polysilicon 31, as shown in Figs. 4B and 4C. In this processing, BHF may be employed for the etching solution. Also, the available etching solution may be a chemical solution of an organic solvent such as IPA 565 with an additional fluorine compound, phosphoric acid-based aqueous solution or sulfuric acid-based aqueous solution. The phosphoric acid may be hot phosphoric acid. By employing

the chemical solution of organic solvent such as IPA with additional fluorine compound, phosphoric acid-based aqueous 570 solution or sulfuric acid-based aqueous solution as the etching solution, the unwanted etching of the device separating region is prevented. After that, the surface of the silicon substrate 10 is rinsed with IPA. The rinse operation removes moisture remained on the surface of the 575 silicon substrate 10, and therefore the generation of the watermark on the surface of the silicon substrate 10 is prevented.

[0054]

The third gate insulating film 38 comprising the first 580 gate insulating film 26 and the high-k insulating film 30 formed on the upper surface thereof, and the fourth insulating film 40 comprising the second gate insulating film 28 and the high-k insulating film 30 formed thereon are manufactured by the processes described above.

585 [0055]

In this embodiment, the surface of the silicon substrate 10 is cleaned at the time when the silicon substrate 10 is exposed just after the third gate insulating film 38 and the fourth gate insulating film 40 are formed, 590 and therefore moisture remained on the surface of the silicon substrate 10 can be sufficiently removed. Therefore, the generation of the watermark on the surface of the silicon substrate 10 is prevented.

[0056]

595 (Third Embodiment)

This embodiment is related to the method for manufacturing the transistor formed in the device separating region. The details will be described by referring Fig. 5A to 5D and Fig. 6A to 6D.

600 [0057]

As shown in Fig. 5A, an oxide insulating film 52 (having a thickness of, for example, 0.8 nm) is formed on a silicon substrate 50 via thermal oxidization, and a high-k insulating film 54 (having a thickness of, for example, 2.0 nm) is deposited via CVD or sputtering thereon, and then a polysilicon layer 56 (having a thickness of, for example, 200 nm) is deposited thereon via CVD.

605 [0058]

Subsequently, as shown in Fig. 5B, a resist material is deposited on the polysilicon layer 56, and the resist material is processed by a lithography technique using ArF excimer laser to form a resist layer 58. Thereafter, the polysilicon layer 56 and the high-k insulating film 54 are selectively etched through the mask of the resist layer 58 to 615 carry out a stepwise removal, as shown in Figs. 5C and 5D. The etching is continued to a halfway to the entire thickness of the high-k insulating film, and thereafter the processing with SPM is carried out.

[0059]

620 Subsequently, the remaining portion of the high-k insulating film 54 and the oxide insulating film 52 are

selectively removed via the wet-etching through the mask of the polysilicon 56 (Figs. 6B and 6C). In this processing, BHF or DHF may be employed for the etching solution. Also, 625 the available etching solution may be a chemical solution of an organic solvent such as IPA with an additional fluorine compound, phosphoric acid-based aqueous solution or sulfuric acid-based aqueous solution or salt thereof. The phosphoric acid may be hot phosphoric acid. The temperature of the 630 chemical solution during the removing processing for the high-k insulating film 54 may preferably be set to be not higher than 200 degree. C, and more preferably not higher than 180 degree. C. The lower limit thereof may be set to be, for example, 40 degree. C, and preferably not lower than 60 635 degree. C. Having these temperature range provides the stable removing processing for the high-k insulating film 54 while inhibiting the surface crazing of the underlying silicon. This configuration may provide a manufacturing of the gate insulating film 60 comprising the oxide insulating 640 film 52 and the high-k insulating film 54.

[0060]

Thereafter, the surface of the silicon substrate 50 is rinsed with IPA. The rinse processing effectively removes the moisture remained on the surface of the silicon substrate 645 50, and therefore the generation of the watermark on the surface of the silicon substrate 50 is prevented.

[0061]

Then, side walls 64 are formed, and thereafter ion

implantation processing is carried out to implant ions into
650 the surface of the silicon substrate 50. Thus, impurity
regions 62 are formed on the both sides of the underlying
portion of the polysilicon layer 56 and gate insulating film
60 by this processing (Fig. 6D). Then, a metallic layer is
formed over the entire surface of the silicon substrate 50,
655 and the portions of the metallic layer contacting the
polysilicon layer 56 and the impurity region 62 are
silicidated, and after that the other portions of the
metallic layer are removed to form a metal silicide layer on
the gate electrode and source-drain regions (not shown). The
660 polysilicon layer 56 may be replaced with poly SiGe for the
gate electrode.

[0062]

When the ion implantation is conducted to the surface
of the silicon substrate 50, moisture remaining on the
665 surface of the silicon substrate 50 may cause a generation of
watermarks, leading an uneven processing condition for the
ion implantation. In this embodiment, moisture is removed
from the surface of the silicon substrate 50 with IPA prior
to carrying out the ion implantation, and thus the impurity
670 region 62 can be formed with an even processing condition.

[0063]

[EXAMPLE]

The example of the present invention will be explained
in the following but the invention is not limited by the
675 example.

[0064]

Similarly as described in the first embodiment with reference to Figs. 1A to 1D and Figs. 2A to 2E, the first gate insulating film 26 and the second gate insulating film 680 28 were formed. In this example, variations in thickness of formed the oxide film in the forming region of the first gate insulating film 26 were measured at respective stages of:

(i) after removing the resist layer 18 with IPA, as shown in Fig. 2A;

685 (ii) after the cleaning processing for the surface of the silicon substrate 10 with APM and DHF, as shown in Fig. 2B; and

(iii) after RTO processing, as shown in Fig. 2C.

The thickness of the film was measured by using ellipsometer.

690 [0065]

In addition, for the purpose of comparison, thickness of formed the oxide film in the forming region of the first gate insulating film 26 was also measured in the case of replacing IPA with SPM for the removal of the resist layer 18 695 in the above stage (i), as a comparative example.

[0066]

Fig. 7 is a graph showing these measurement results. In the stage (i), i.e., after the removal of the resist layer 18, no oxide layer was formed on the surface of the silicon 700 substrate 10 when IPA was used. On the contrary, in the comparative example, a chemical oxide film having film thickness of 1.2 nm was formed on the surface of the silicon

substrate 10 when SPM was used. Thereafter, in the stage (ii), when the cleaning with APM and DHF was conducted, 705 formation an oxide film having a thickness of about 0.9 nm on the surface of the silicon substrate 10 was confirmed, even if the removal of the resist layer 18 in the stage (i) had been conducted with IPA. Subsequently, when RTO processing was conducted in the stage (iii), the generated chemical 710 oxide film shrunk to a certain level. When RTO processing was conducted for the silicon substrate on which the removal of the resist layer 18 was conducted with IPA in the stage (i), the thickness of the unwanted chemical oxide film after the stage (iii) was 0.8 nm. On the contrary, when RTO 715 processing was conducted for the comparative silicon substrate on which the removal was conducted with SPM in the stage (i), the thickness of the chemical oxide film after the stage (iii) was 1.0 nm. As such, it was confirmed that the removal processing of the resist layer 18 with IPA was 720 effective in reducing the thickness of the resultant first gate insulating film 26 including the chemical oxide film by about 0.2 nm by comparison with the comparative example including the removal processing of the resist layer 18 with SPM. Further evaluations of the repeated testing were 725 conducted to provide that the controlling the thickness of the resultant first gate insulating film 26 with higher reproducibility.

[0067]

As mentioned above, it is confirmed that the thickness

730 of the first gate insulating film 26 depends on the thickness
of the oxide film formed during the removal of the resist
layer 18 and the thickness of the oxide film formed during
the cleaning of the silicon substrate 10 with APM and DHF.
When the conventional manner of removing the resist layer 18
735 with SPM is employed, thicker oxide film is formed on the
surface of the silicon substrate 10 during the removing
processing of the resist layer 18, due to the influence of
SPM. On the contrary, when the manner of removing the resist
layer 18 with IPA is employed, no oxide film is formed on the
740 surface of the silicon substrate 10 during the removing
processing of the resist layer 18. Therefore, the thickness
of the eventually obtained first gate insulating film 26 can
be reduced by employing IPA for removing the resist layer 18,
as compared with the case of employing SPM.

745 [0068]

[ADVANTAGE OF THE INVENTION]

According to the present invention, there is provided
the technology of controlling the thickness of the silicon
oxide film formed on the semiconductor substrate to be
750 thinner is provided. According to the present invention,
there is provided the technology for preventing the formation
of the unwanted film or the stain such as watermark on the
semiconductor substrate. According to the invention, there
is provided the technology of controlling the uniformity of
755 the film formed on the semiconductor substrate.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[Fig. 1]

A schematic sectional view of the semiconductor substrate, showing an example of the processing steps 760 described in the first embodiment according to the present invention.

[Fig. 2]

A schematic sectional view of the semiconductor substrate, showing an example of the processing steps 765 described in the first embodiment according to the present invention.

[Fig. 3]

A schematic sectional view of the semiconductor substrate, showing an example of the processing steps 770 described in the second embodiment according to the present invention.

[Fig. 4]

A schematic sectional view of the semiconductor substrate, showing an example of the processing steps 775 described in the second embodiment according to the present invention.

[Fig. 5]

A schematic sectional view of the semiconductor substrate, showing an example of the processing steps 780 described in the third embodiment according to the present invention.

[Fig. 6]

A schematic sectional view of the semiconductor

substrate, showing an example of the processing steps
785 described in the third embodiment according to the present
invention.

[Fig. 7]

A graph of the film thickness of the oxide films of
IPA-cleaned and SPM-cleaned, showing the variation of the
790 thickness in the respective process steps.

[Fig. 8]

A schematic sectional view of the semiconductor
substrate, showing an example of the prior art processing
steps.

795 [Fig. 9]

A schematic sectional view of the semiconductor
substrate, showing an example of the prior art processing
steps.

[REFERENCE NUMERALS]

800 10 silicon substrate
12 device separating region
13a first region
13b second region
14 first oxide film
805 16 second oxide film
18 resist layer
20 chemical oxide film
22 third oxide film
26 first gate insulating film
810 28 second gate insulating film

30 high-k insulating film
31 polysilicon
32 resist layer
38 third gate insulating fil
815 40 fourth gate insulating film
50 silicon substrate
52 oxide insulating film
54 high-k insulating film
56 polysilicon layer
820 58 resist layer
60 gate insulating film
62 impurity region
64 side wall

[DOCUMENT] ABSTRACT OF THE DISCLOSURE

[ABSTRACT]

[OBJECT] A film thickness of a gate insulating film is properly controlled.

5 [MEANS TO SOLVE THE PROBLEM] A first oxide film (not shown) and a second oxide film 16 are formed in a first region 13a and a second region 13b, respectively, on the surface of the semiconductor substrate 10, via thermal oxidization method, and the first oxide film is removed while the second oxide 10 film 16 is covered with the resist layer 18 formed thereon, and then the resist layer 18 is removed with a chemical solution containing an organic solvent such as isopropyl alcohol as a main component. Subsequently, a third oxide film 22 having different thickness than the second oxide film 15 16 is formed in the first region 13a.

[REPRESENTATIVE DRAWING] FIG. 2



[DOCUMENT] Drawings

Fig.1

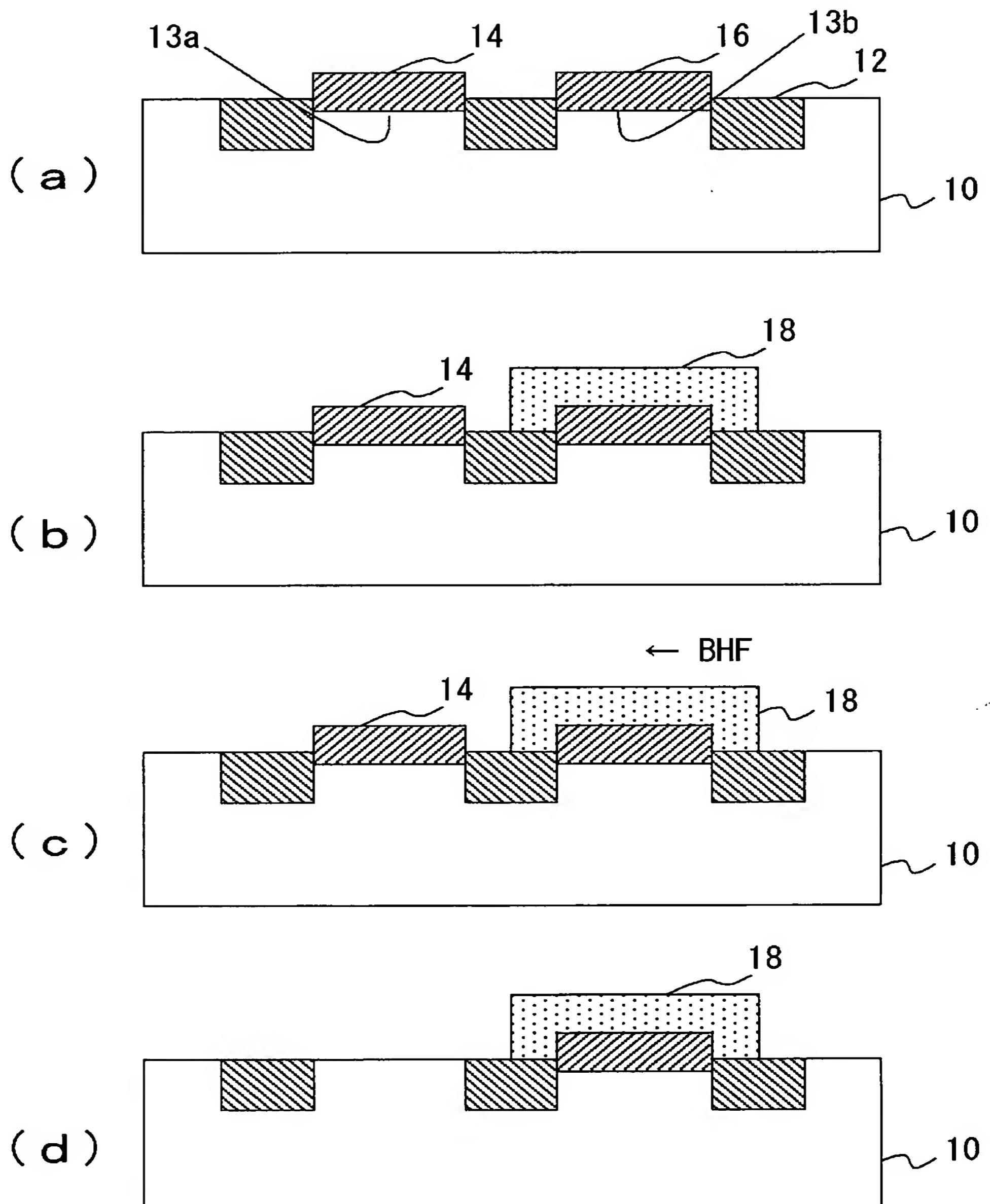


Fig.2

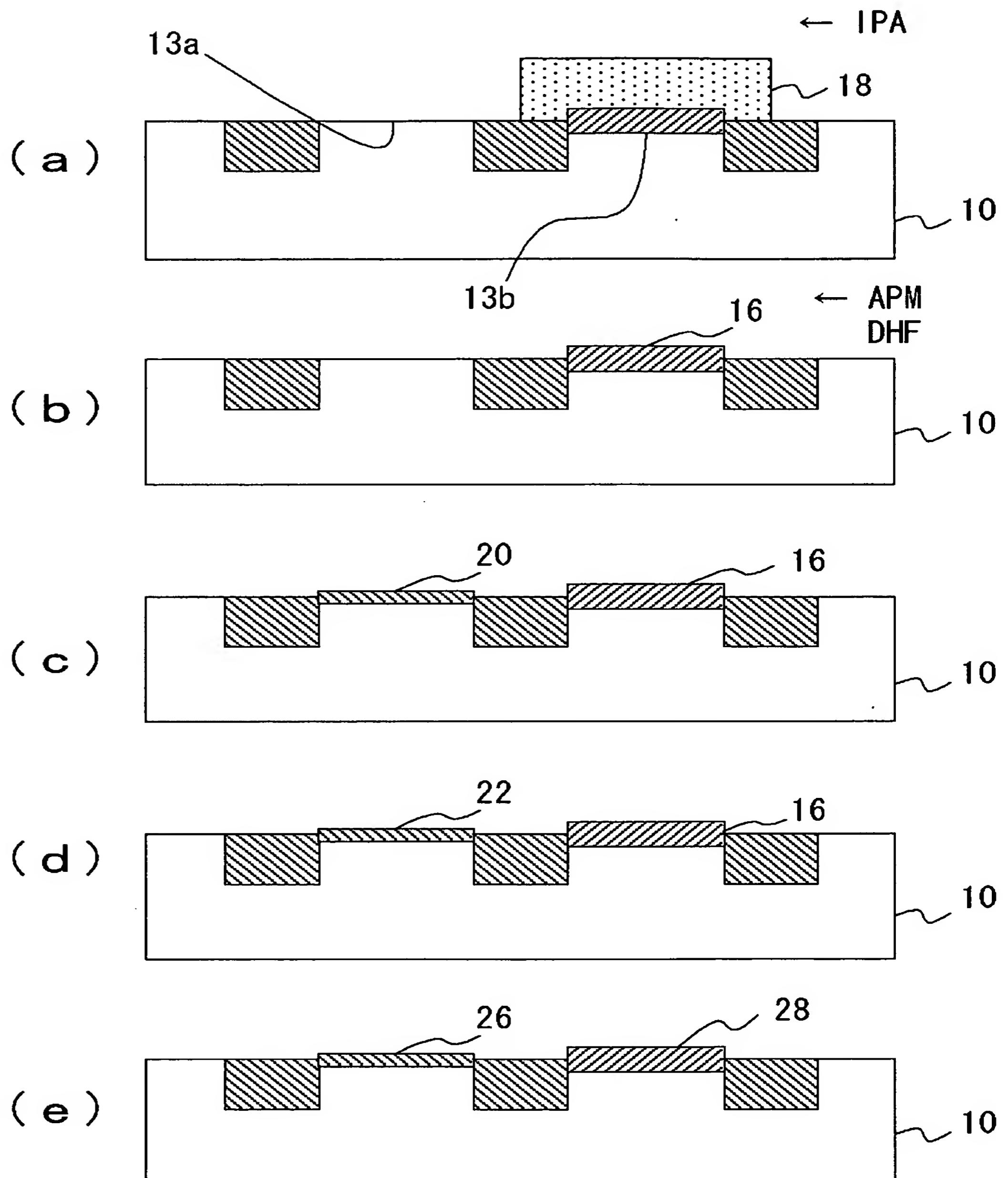


Fig.3

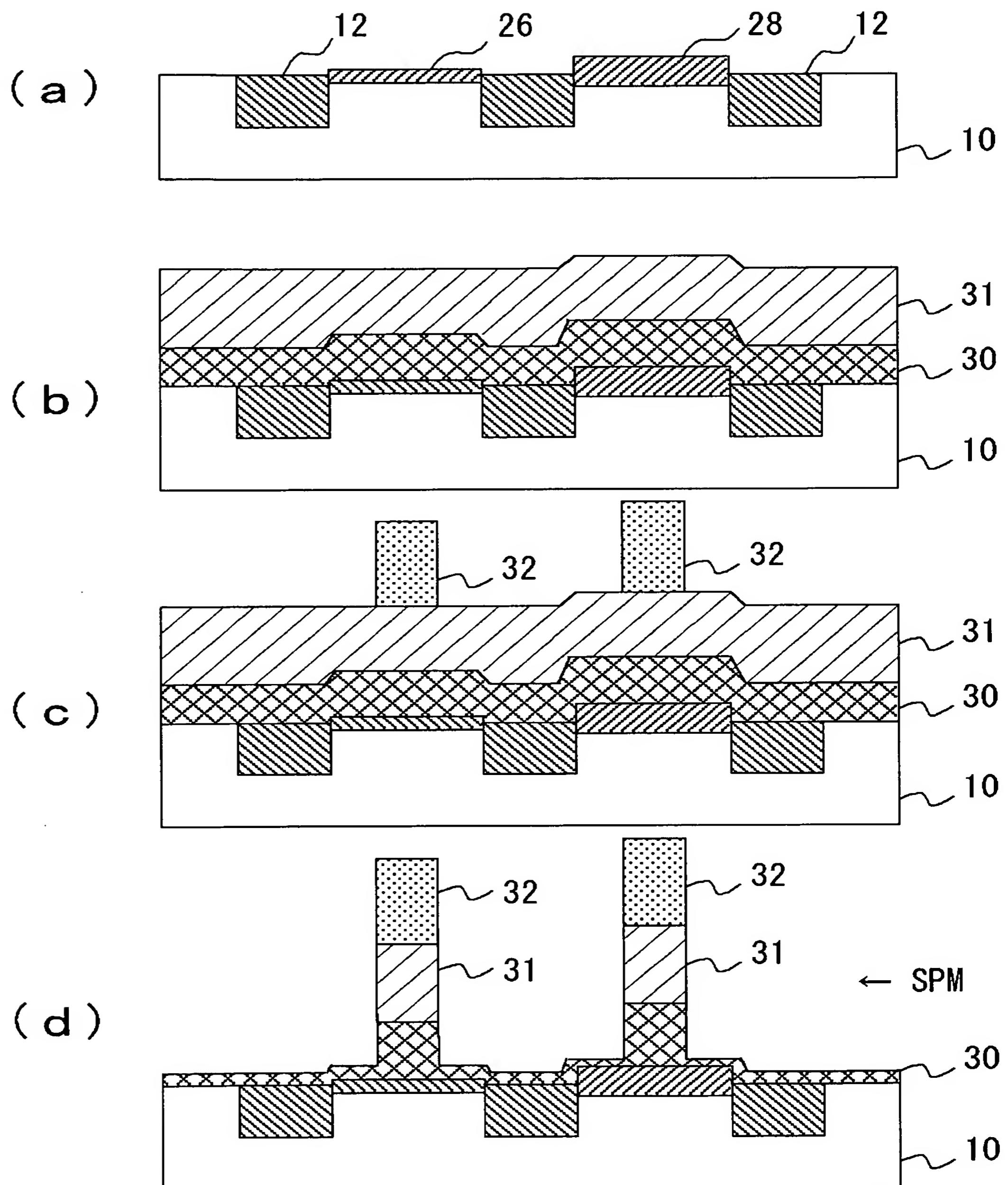


Fig.4

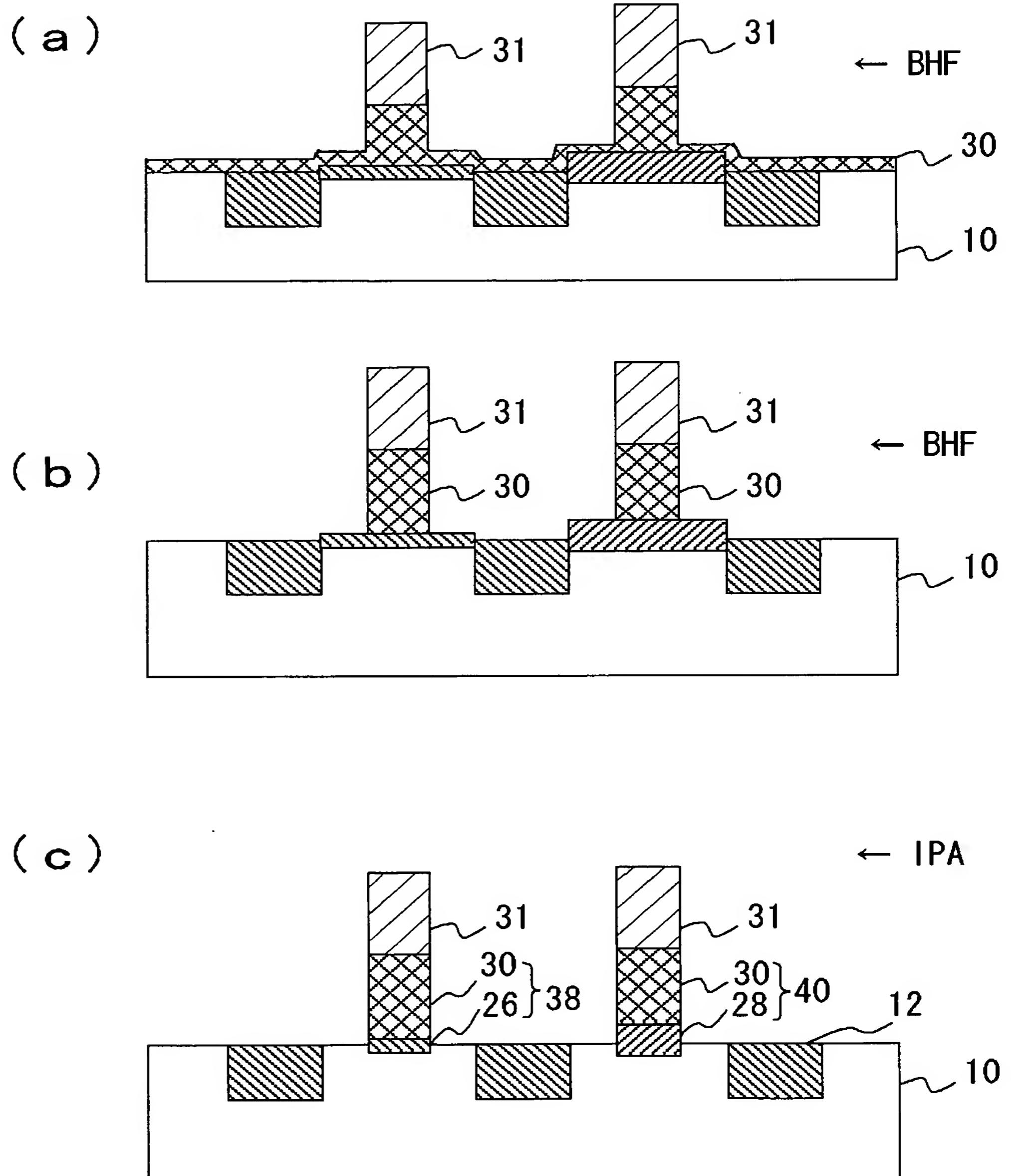


Fig.5

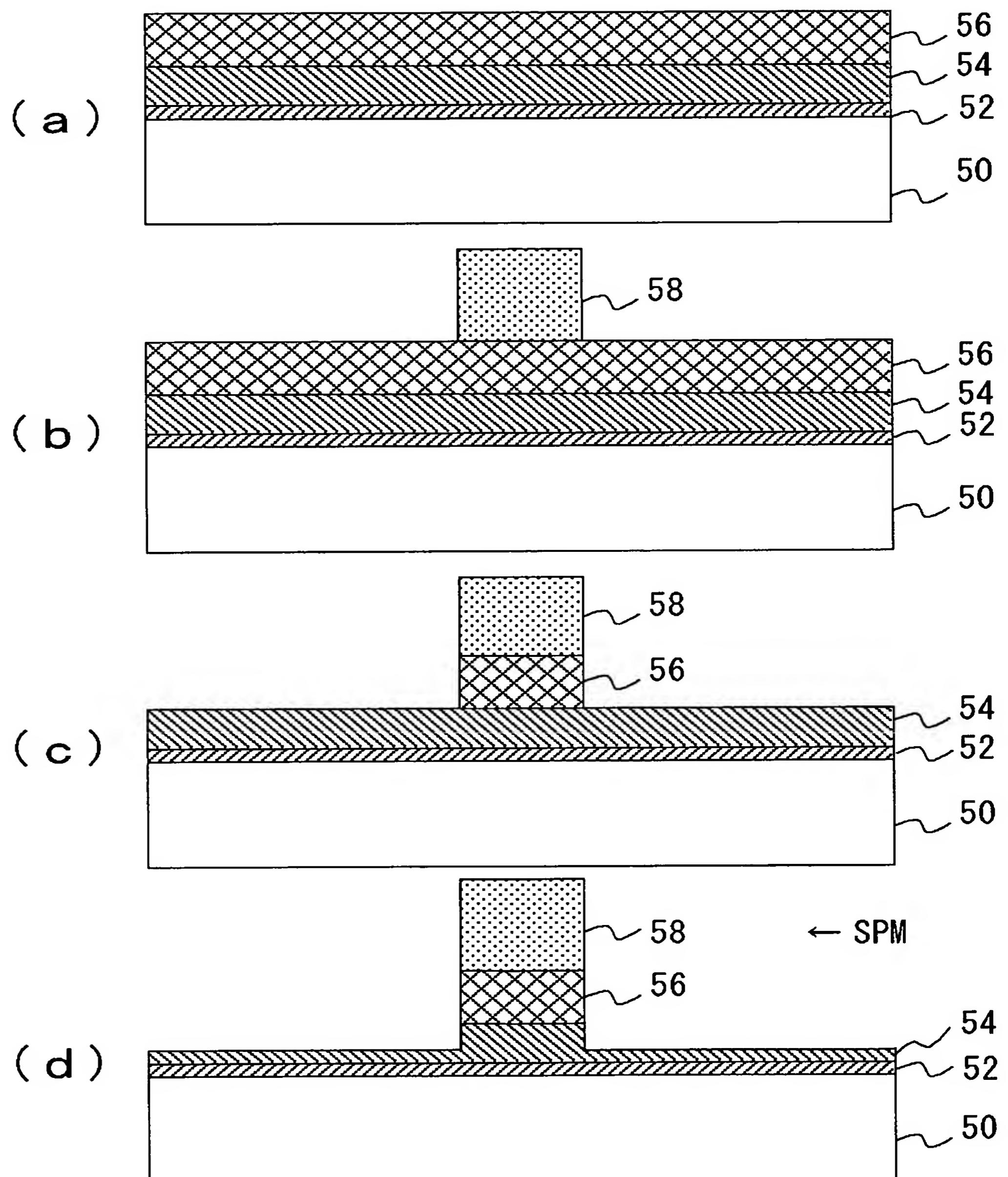


Fig.6

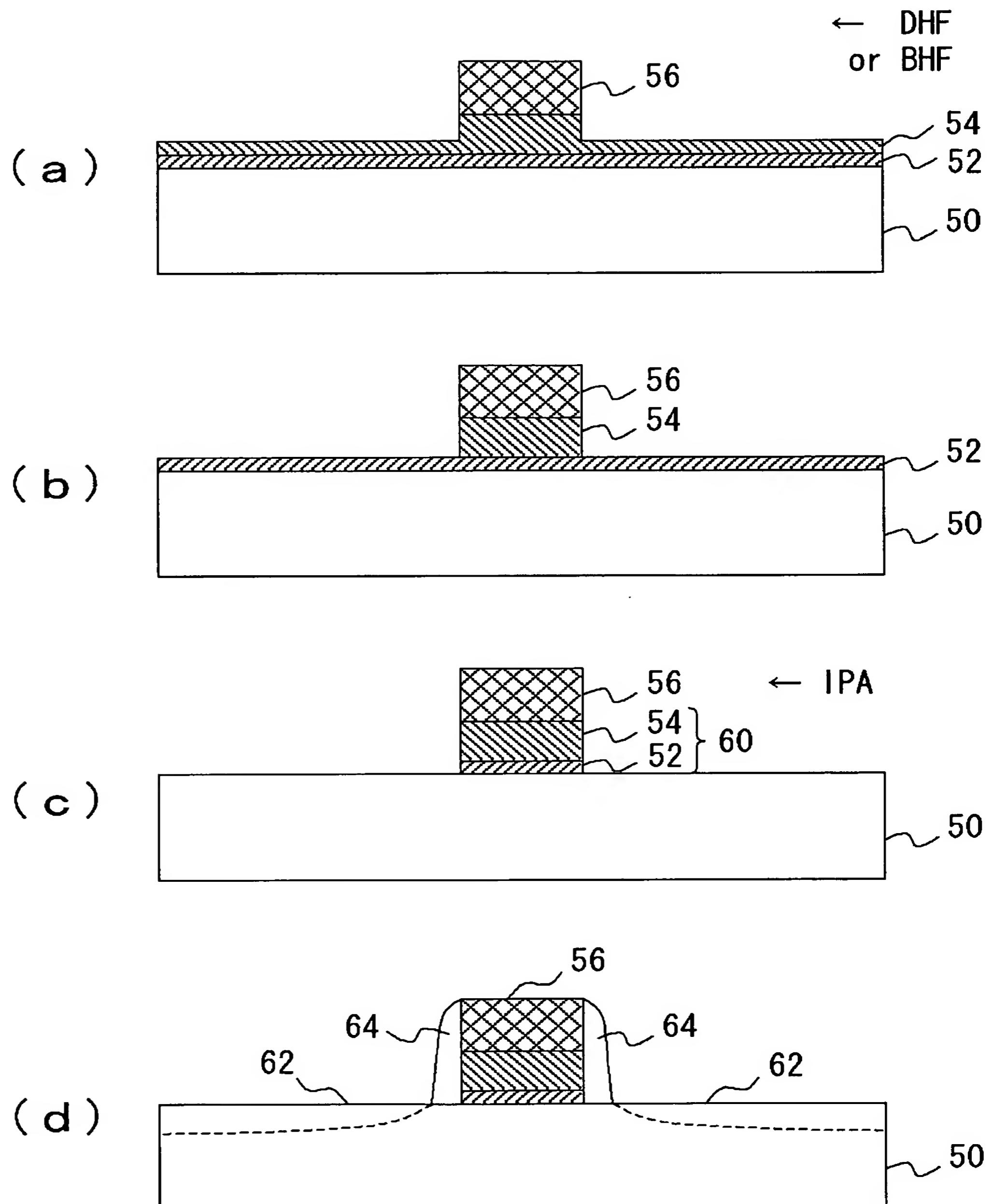
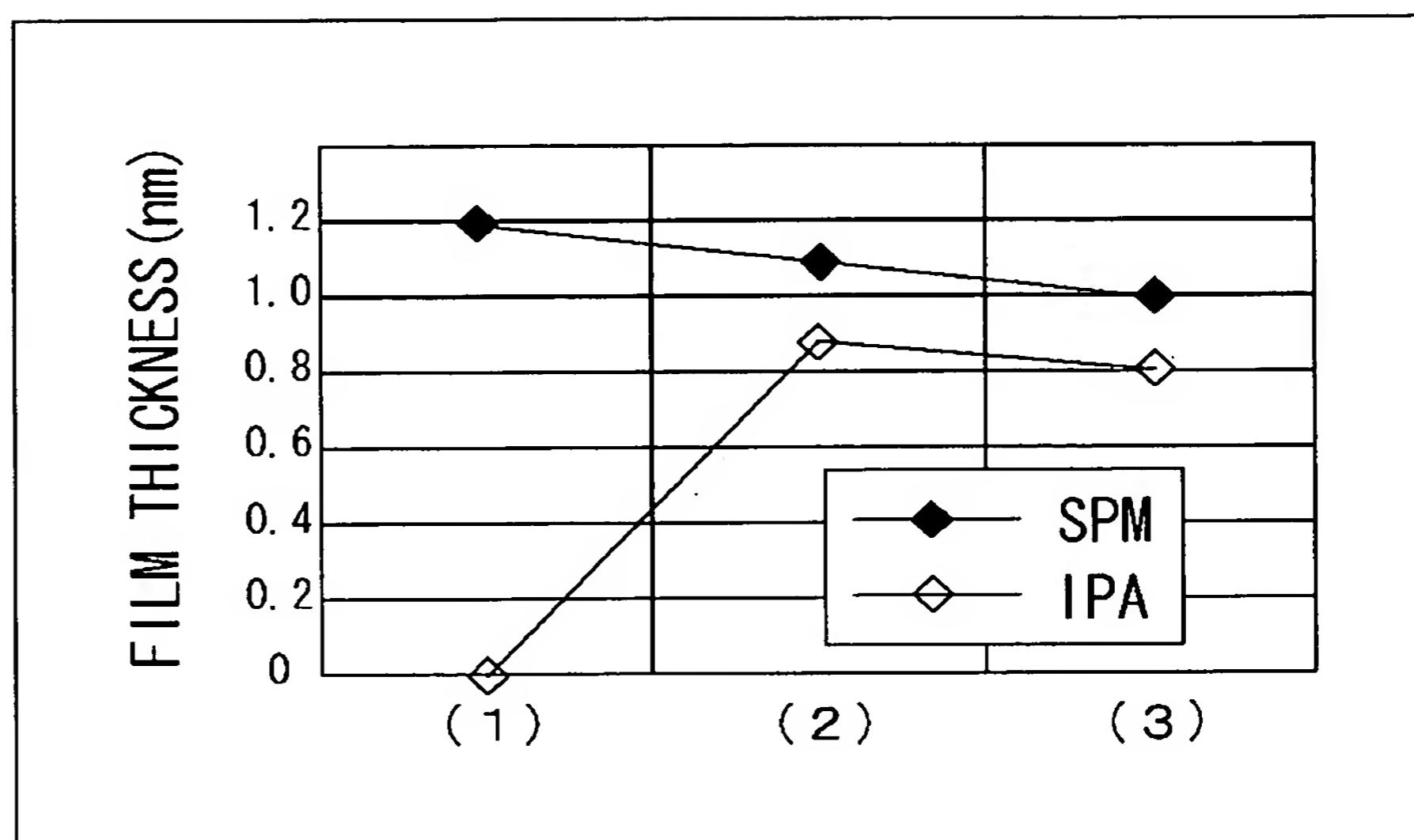


Fig.7



- (1) AFTER REMOVING RESIST LAYER
- (2) AFTER APM/DHF CLEANING
- (3) AFTER THERMAL OXIDIZATION

Fig.8

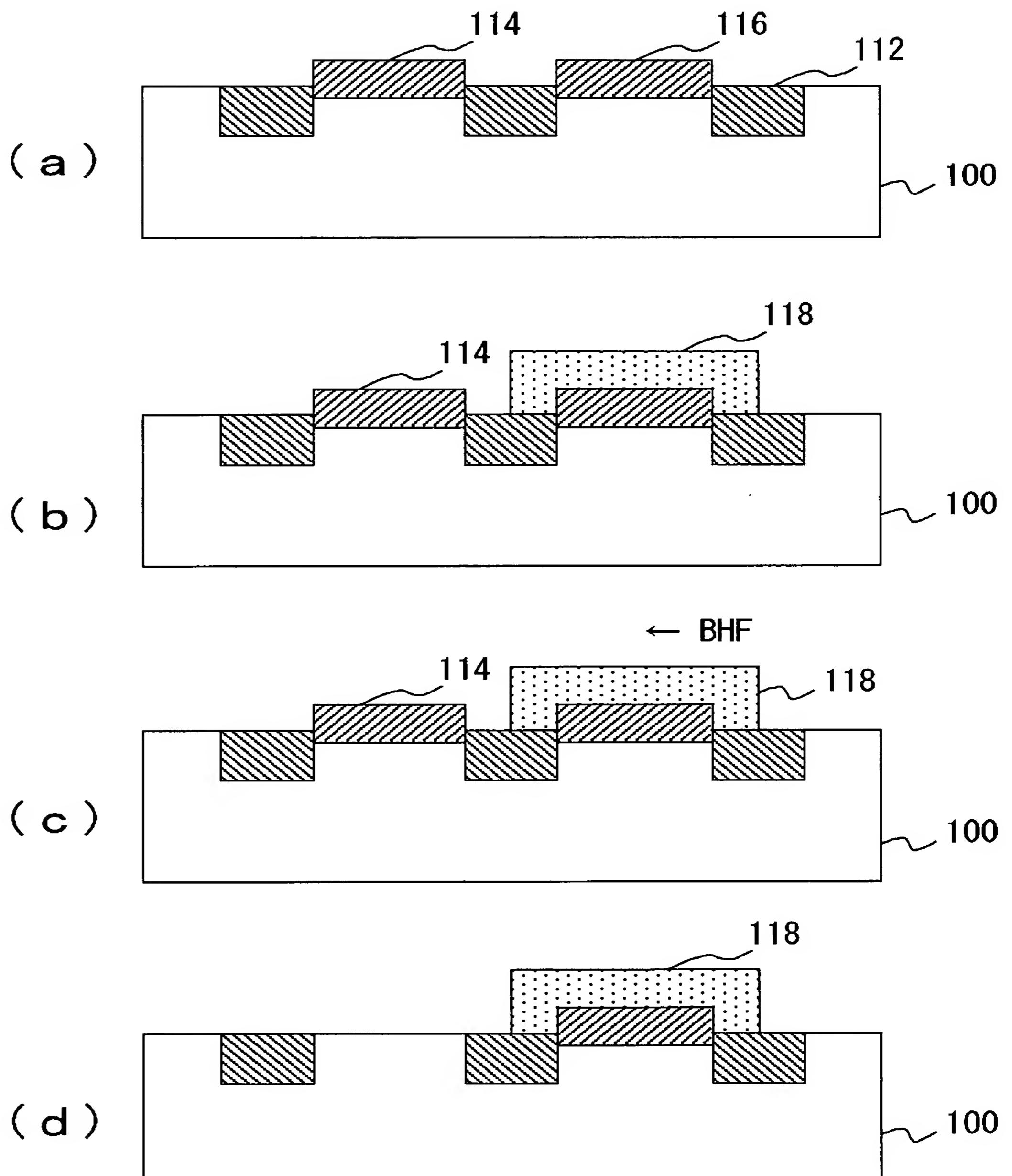


Fig.9

